



Host Institution:

**PETRU PONI Institute of Macromolecular Chemistry of
Romanian Academy**

41-A, Grigore Ghica Voda Alley, 700487 Iași, Romania

Contracting Authority:

**Executive Unit for Financing Higher Education
Research Development and Innovation**

Romania

EXPLORATORY RESEARCH PROJECT

PN-II-ID-PCE-2011-3-0199

Contract nr. 300/05.10.2011

POLYMER MATERIALS WITH SMART PROPERTIES

- 2015 -

Research Team:

Dr. Simona Morariu

Dr. Madalina-Luiza Gradinaru

Dr. Mirela Teodorescu

Dr. Aurora Chiriac

Dr. Cristina-Eliza Brunchi

Dr. Luminita Ghimici

Project Leader,

Dr. Maria Bercea

BRIEF REPORT

concerning the results obtained by project team between December 16, 2014 – December 15, 2015

Objective: **Constitutive response of the obtained materials in different using conditions**

Associated Activities:

- 1. Correlation between the thermodynamic properties and rheological data; establishing the conditions in which the supramolecular structures appear**
- 2. Correlation between the thermodynamic parameters and phase separation phenomena**

1. Correlation between the thermodynamic properties and rheological data; establishing the conditions in which the supramolecular structures appear

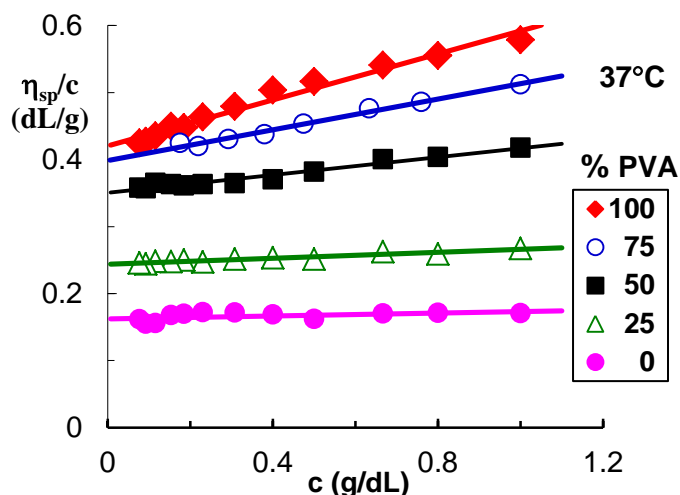
The ability of polymers to form supramolecular structures as a response to external stimuli such as: temperature, pH, electric field, magnetic field, or a combination of these stimuli, represents a challenge for researchers in the present. If the polymer system has the ability to return to its original state when the external stimulus ceases, then it presents a particularly interest for the development of new materials with smart properties. Until now different strategies were developed for the elaboration of materials with response to external stimuli, using both natural and synthetic polymers, sometimes with the addition of clays or other inorganic materials, depending on the purpose. Physical hydrogels obtained from aqueous solutions are of particular interest due to the fact that they do not require the use of toxic crosslinkers, and in many cases the sol-gel transition is reversible. Chemical hydrogels are preferred for applications requiring the stability of the network structure in time, under various pH conditions or in different chemical environments.

Scientific investigations carried out in the project were focused on the obtaining of hydrogels based on poly(vinyl alcohol) (PVA) with responses to external stimuli (temperature, pH) starting from: mixtures of synthetic polymers (PVA/Pluronic F127); mixtures of synthetic/natural polymers (PVA/Chitosan); polyurethanes with special structures. Most of the results were included in published papers or articles in press, and this report briefly presents the most relevant results obtained for the mixtures that were mentioned.

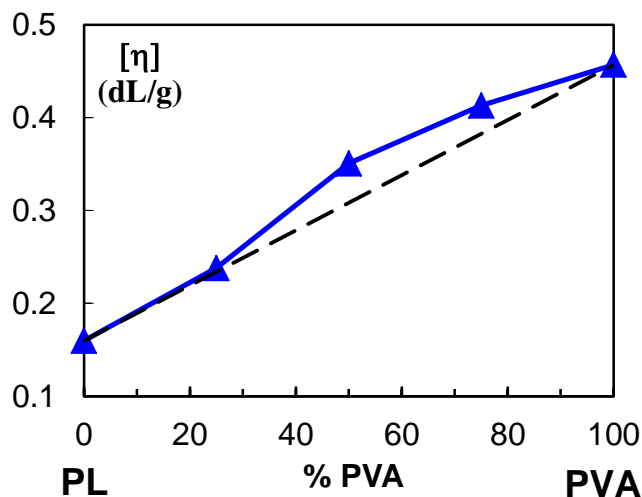
Mixtures of PVA and Pluronic F127 (PL) were investigated by viscometry, rheology, dynamic light scattering and zeta potential measurements, in order to understand the interactions between these two polymers in aqueous solution and the optimal conditions for obtaining thermosensitive hydrogels [1, 2].

Figure 1 shows the dependences between reduced viscosity and polymer concentration (c) and the variation of intrinsic viscosity obtained from these plots (using Huggins method) with the composition of the PL/PVA mixture. For a PVA content greater than 25% in the PL/PVA mixtures, intrinsic viscosity values are superior to those resulted from additive rule (dashed line in Fig 1b). This could be due to the interactions between different macromolecules (PVA chains with PL chains), or macromolecules of the same type.

It was shown that in aqueous solutions PL chains form micelles [2-4] where hydrophilic part (PEO) is the outer shell, while hydrophobic part (PPO) is „the core”. PVA chains in aqueous solution interact with each other through hydrogen bonds formed between –OH groups along the macromolecules [5,6]. Huggins constant was greater than 0.5 for the mixtures containing 50% and 75% PVA, suggesting the polymers trend to form clusters and aggregates. These observations led to the elaboration of thermosensitive hydrogels based on PL/PVA mixtures.



(a)



(b)

Figure 1. (a) The dependence between reduced viscosity (η_{sp}/c) and total concentration of the polymer and (b) intrinsic viscosity ($[\eta]$) variation as a function of the PL/PVA mixture composition in aqueous solution at 37°C [1].

PL, PVA samples and mixtures with 25%, 50% and 75% PVA having a total polymer concentration of 15% were prepared and stored in a refrigerator. Samples were placed into the rheometer geometry at 4°C and then subjected to heating at controlled heating rate.

Figure 2 shows the evolution of the elastic modulus (G'), the viscous modulus (G'') and the loss tangent ($\tan \delta = G''/G'$) as a function of temperature for a 50% PVA/50% PL mixture at a heating rate of 0.5°C/min, keeping constant the shear parameters (1 Pa, 1 rad/s). In these conditions, the sol-gel transition occurs at 32.8°C; at lower temperatures the viscoelastic behavior is typical to viscous fluids ($G' < G''$, $\tan \delta > 1$), and at temperatures higher than 32.8°C the viscoelastic behavior is typical to elastic solids ($G' > G''$, $\tan \delta < 1$).

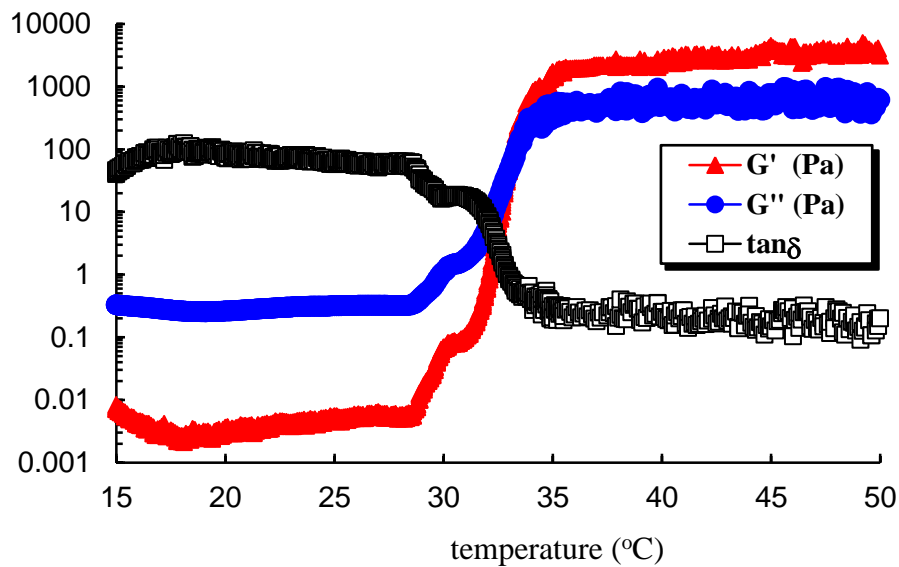


Figure 2. The evolution of the viscoelastic parameters for a 15% polymer sample with the composition of 50% PL and 50% PVA [1].

The temperature at which the sol-gel transition occurs and the characteristics of the obtained hydrogels depends both on the composition of the PL/PVA mixture, as well as thermal history of the sample, as can be seen from the data presented in Table 1 and Table 2.

Table 1. Sol-gel transition temperature observed from the rheological measurements for PL/PVA mixtures in aqueous solution (15% total polymer concentration) at different heating rates [1].

| Sample (%PVA) | Sol-gel transition temperature (°C) | | |
|------------------|--|---------|---------|
| | 0.5°C/min | 1°C/min | 2°C/min |
| 0 (PL) | 27.8 | 28.1 | 30.6 |
| 25 | 32.2 | 35.1 | 42.8 |
| 50 | 32.8 | 35.9 | 44.7 |
| 75 | 33.2 | 37.1 | 48.0 |
| 100 (PVA) | 28.7 | 32.6 | 42.9* |

*For PVA solution subjected to a heating rate of 2°C/min it was observed an increase of the viscoelastic moduli at 42.9°C, but the sol-gel transition did not occur in the investigated temperature domain, the sample maintaining its character as a viscous fluid ($G' < G''$).

Table 2. The influence of the heating rate on the viscoelastic characteristics of the obtained hydrogels (G'_{∞} , G''_{∞} and G''_{∞}/G'_{∞}) at 37 °C, 1 Pa and 1 rad/s [1].

| Sample (% PVA) | 0.5 °C/min | | | 1 °C/min | | | 2 °C/min | | |
|-------------------|-----------------------|------------------------|----------------------------|-----------------------|------------------------|----------------------------|-----------------------|------------------------|----------------------------|
| | G'_{∞} (Pa) | G''_{∞} (Pa) | G''_{∞}/G'_{∞} | G'_{∞} (Pa) | G''_{∞} (Pa) | G''_{∞}/G'_{∞} | G'_{∞} (Pa) | G''_{∞} (Pa) | G''_{∞}/G'_{∞} |
| 0 (PL) | 760 | 157 | 0.206 | 258 | 87.4 | 0.339 | 115 | 51 | 0.443 |
| 25 | 1518 | 400 | 0.264 | 175 | 74 | 0.423 | 136 | 69 | 0.507 |
| 50 | 1388 | 370 | 0.266 | 1076 | 439 | 0.408 | 145 | 86 | 0.593 |
| 75 | 3790 | 816 | 0.216 | 965 | 337 | 0.349 | 484 | 208 | 0.430 |
| 100 (PVA) | 72 | 33.5 | 0.465 | 31.1 | 27.2 | 0.875 | 0.791 | 1.90 | 2.402 |

All rheological measurements were performed in the linear viscoelasticity domain which was established by preliminary amplitude sweep tests. Stability in time for the networks formed at 37°C was followed in frequency sweep tests performed at different time intervals after the refrigerated sample at 4°C was heated to 37°C. In Figure 3 are shown, as an example, the results obtained after the 50% PVA sample was thermostatted for 10 and 60 minutes at 37°C.

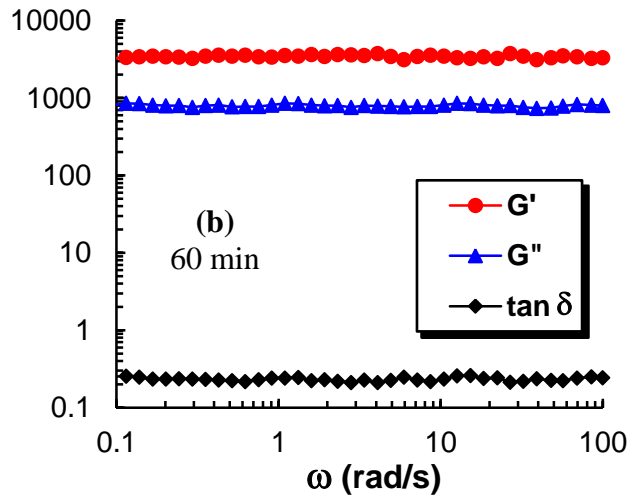
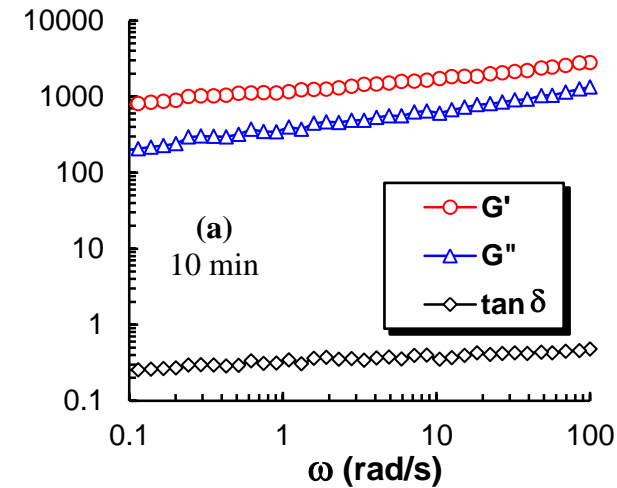


Figure 3. The evolution of the viscoelastic parameters as a function of the oscillation frequency for a 50% PL and 50% PVA mixture after being kept at 37°C for 10 minutes (a) and 60 minutes (b) [1].

After a short resting period at 37°C (10 minutes), both viscoelastic moduli indicate a slight dependence on the oscillation frequency, suggesting that the network structure formation is still evolving. After a longer resting period (60 minutes) it is observed that the physical network is formed, the viscoelastic parameters are now independent of the oscillation frequency and do not evolve in time (Figure 4). This evolution in the first 60 minutes of heating was observed only for PVA mixtures. For PL the transition occurs very rapidly (fractions of a second) and the gel structure is formed in the first 100 seconds of heating the sample at 37°C, and the stationary state is reached after approx. 1200 seconds.

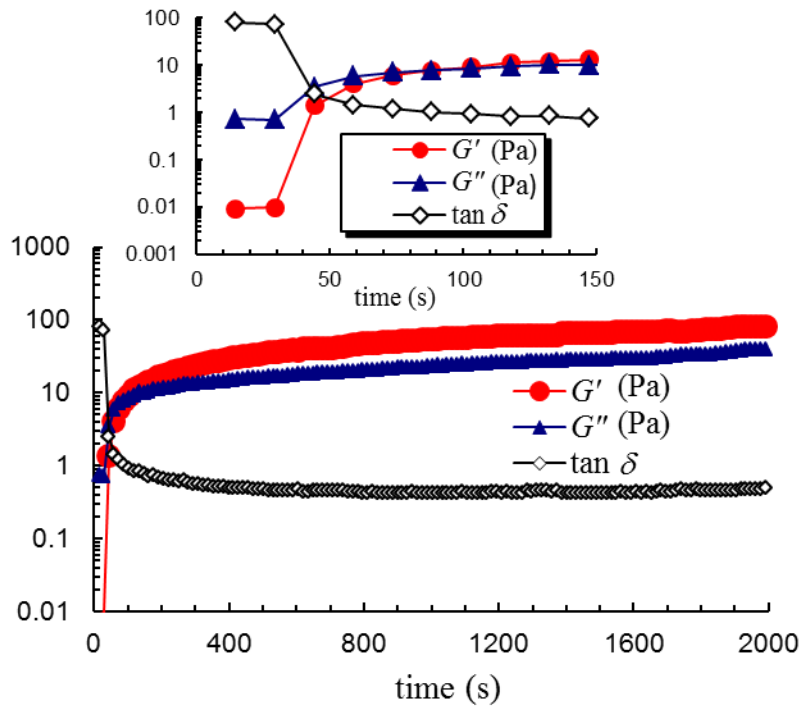


Figure 4. The evolution of the gelling process at 37°C for a 75% PVA mixture [2].

In the presence of bovine serum albumin (BSA), the sol-gel transition is delayed, showing a sharp variation of the viscoelastic properties after approx. 800 s (Figure 5).

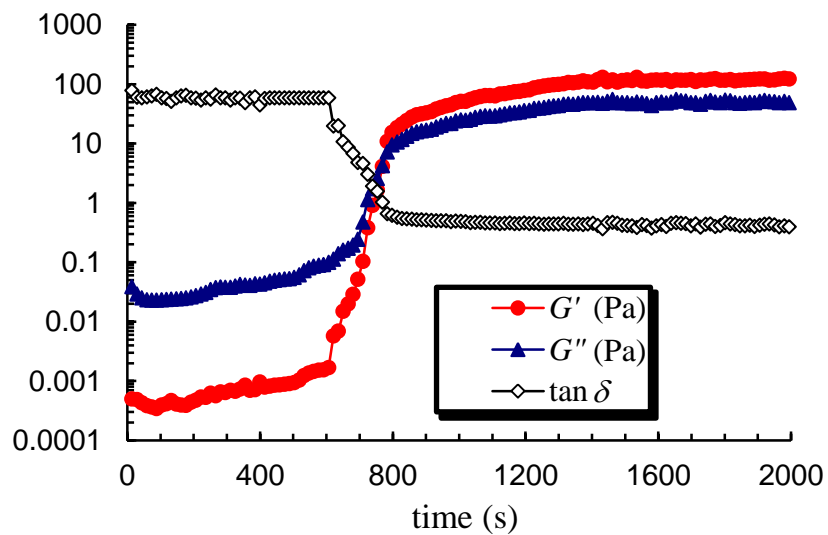


Figure 5. The evolution of the gelling process at 37°C for 75% PVA mixture in the presence of BSA (BSA/polymer weight ratio = 1/1) [2].

This behavior is explained by hydrophobic interactions between PPO and PL sequences and BSA that prevents the formation of block copolymer micelles. The same observation was reported in the literature by Guo et al. [7] who investigated by fluorescence spectroscopy the micellization in the presence of BSA of the PEO-PPO-PEO type block copolymers with different content of PPO. It was observed that the addition of BSA in the solutions of copolymer (Pluronic type) moves the critical micellization temperature at higher values. For higher concentrations of Pluronic copolymer, the self-assembling of the micelles is delayed and the gelling is completely compromised for high amount of PPO in copolymer or BSA in the mixture.

In the case of PL/PVA mixtures dimensional changes are observed at the appearance of the supramolecular structures due to the competition between different types of interactions (hydrophil/hydrophob, hydrogen bonds) and thermal motion (Figure 6).

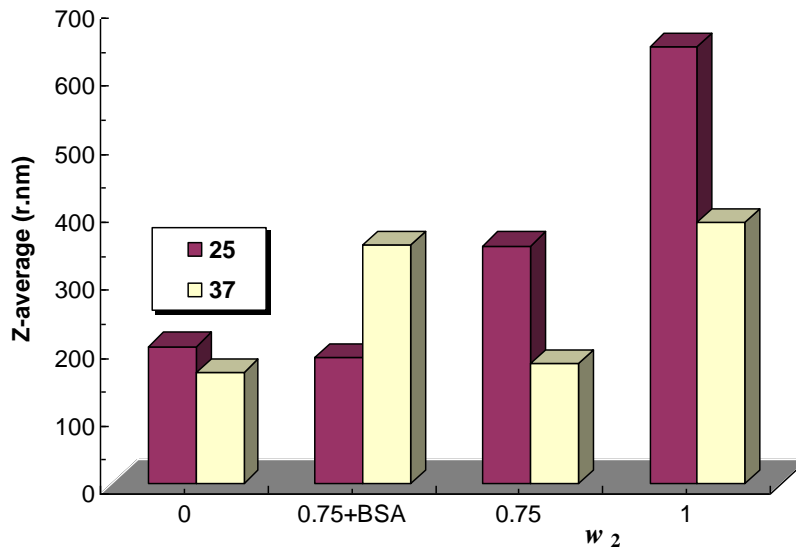


Figure 6. Particle dimensions determined at 25°C and 37°C for PL, PVA and 75% PVA mixture in the presence and absence of BSA [2].

Electrophoretic mobility (μ), determined with Malvern Zetasizer ZS at different temperatures, allowed the calculation of zeta potential, ζ , using Henry – Smoluchowski approximation:

$$\zeta = \frac{\eta\mu}{\varepsilon} \quad (1)$$

where η is the viscosity and ε is the dielectric constant of the medium.

The investigated PL/PVA/water systems have values of ζ between -2.5 mV and 2 mV, showing a strong tendency of formation of supramolecular structure (Figure 7). The effect of temperature on the ζ parameter varies with the mixture composition. For mixtures of aprox. 55% PVA, the increase of temperature determines a slight decrease of zeta potential, and for mixtures with high amount of PVA the zeta potential slowly increases with temperature. The addition of BSA in the PL/PVA mixtures determines the changing of the ζ parameter sign from negative to positive values.

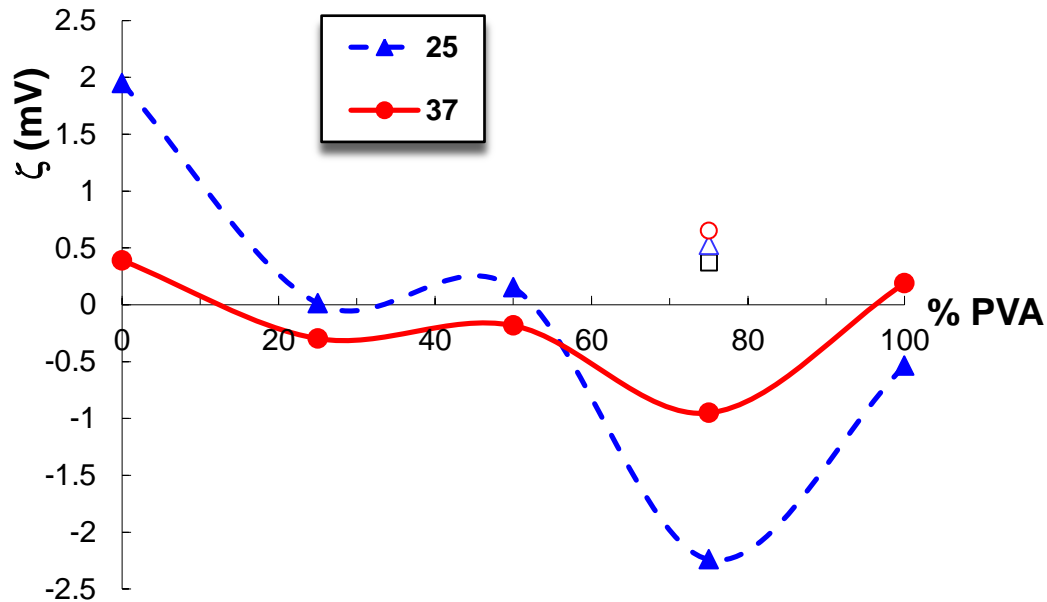


Figure 7. The zeta potential as a function of the PL/PVA mixture composition (full symbols) at the temperatures (°C) shown in the Figure. Open symbols show the values obtained in the presence of BSA.

The influence of temperature on the conductivity of the PL/PVA mixtures is illustrated in Figure 8. The conductivity of the mixtures with a higher amount of PL and of the mixture with BSA is more sensitive to temperature change as compared with the samples with higher PVA concentration.

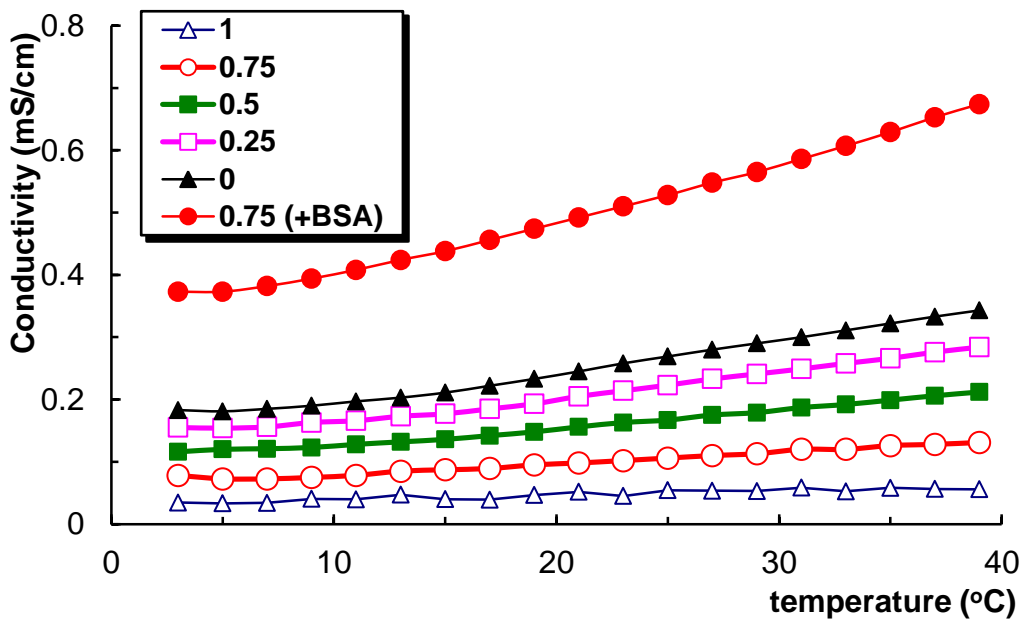


Figure 8. The conductivity as a function of temperature for different compositions of PL/PVA mixture and for 75% PVA mixture in the presence of BSA (BSA/polymer weight ratio = 1/1).

The investigations performed for PL/PVA mixtures in water showed that the thermodynamic and electrokinetic properties significantly influence the formation of supramolecular structures. Analysis of rheological parameters allowed the identification of the optimal conditions for the formation of gels with thermoreversible structure

The obtained results suggest that at low temperatures the PL/PVA mixtures are in homogenous solution state where PL micelles coexist with PVA chains. At the increase of temperature, hydrophobic interactions become dominant and favor the formation of the gel structures. In such networks, the PL polymicelles interact with long chains of PVA through hydrogen bonds between $-OH$ groups of PVA and PEO blocks in the PL copolymer structure (Figure 9) [2]. The presence of multiple PVA macromolecules gives stability to PL micelles, enhanced characteristics such as superior mechanical properties and a weaker tendency to dissolve in aqueous medium.

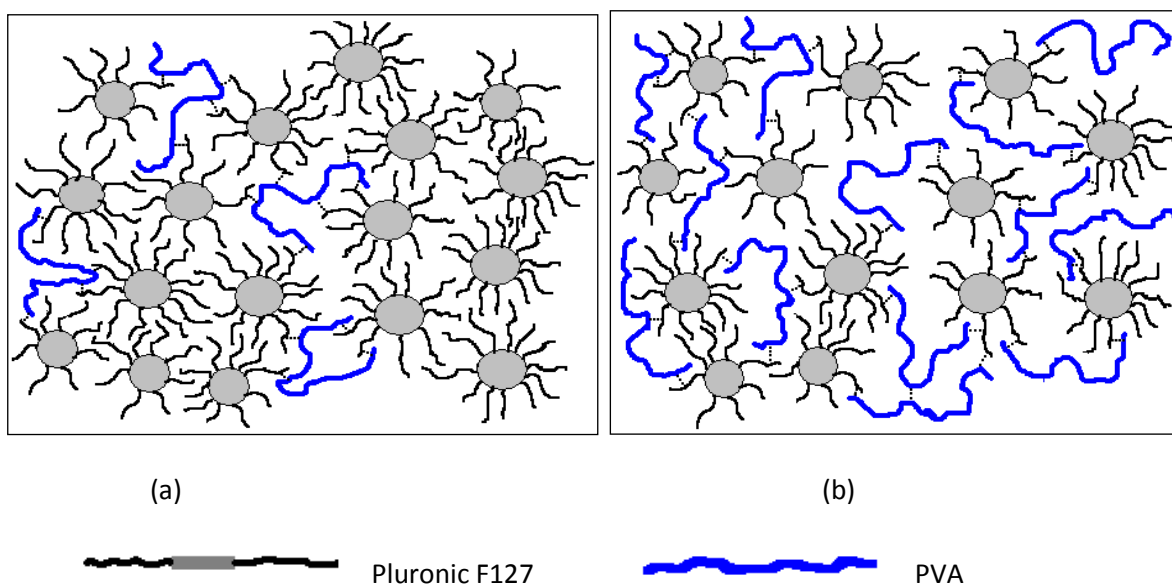


Figure 8. Schematic representation of the hydrogel structure formed from PL/PVA mixtures for: (a) low content of PVA; (b) high content of PVA [2].

A remarkable property of the hydrogels obtained in this phase of the research project is the high elasticity reflected by the elastic modulus value (influenced by the structuring degree of the sample), as well as the high degree of elastic recovery observed in the creep tests and elastic recovery tests. For example, in Figure 9 are presented the creep and elastic recovery curves for a polyurethane sample with potential applications in biomaterials field [8]. The recovery degree of the elasticity is higher than 90% for the hydrogel successively subjected to the action of a shear stress (creep) over different periods of time, and the history of deformation do not influence the sample behavior. Figure 10 shows the elastic recovery degree for chitosan/PVA mixtures in the presence of anionic clay of MgAlLDH type, for physical networks [9] and for chemically crosslinked hydrogels [10].

For these types of materials, the pH sensitivity can be observed: chemical networks show the maximum degree of elastic recovery at pH = 5.5 [10], and the physical networks for neutral or basic pH [9]. The behavior is dictated both by physico-chemical characteristics of the clay (for which basic medium is favorable), as well as the chitosan particularities (sensitive to acid pH [11], precipitates in basic medium).

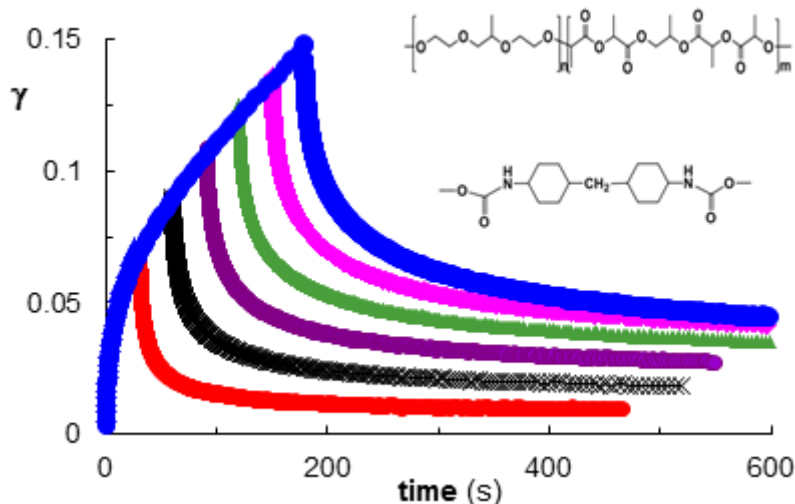


Figure 9. Creep and elastic recovery curves obtained for a polyurethane sample at 37°C [8].

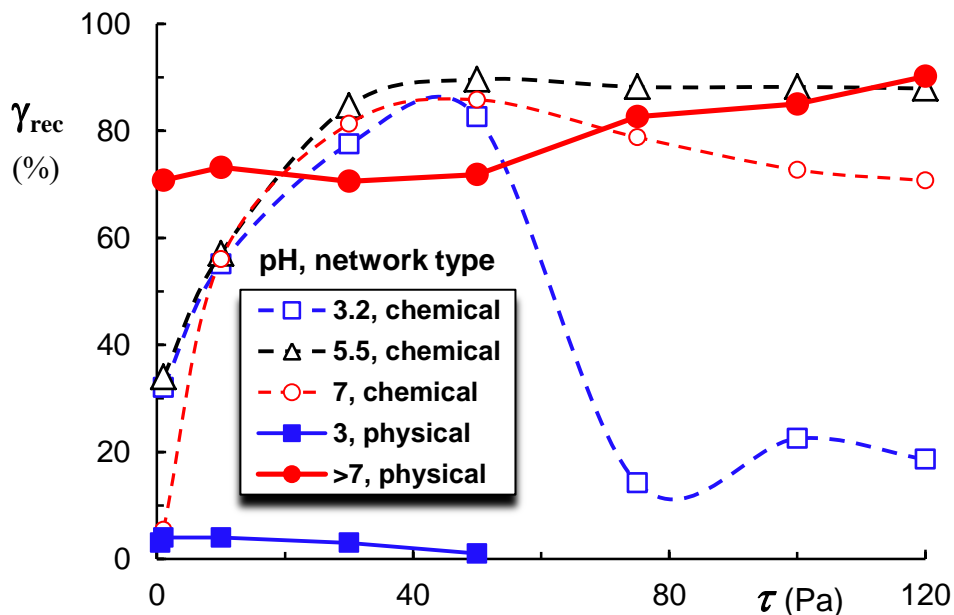


Figure 10. The elastic recovery degree of the deformation for physically crosslinked (full symbols, continuous line) [9] or chemically crosslinked (open symbols, dashed line) [10] chitosan/PVA/LDH mixtures, at different pH values of the environment.

2. Correlation between the thermodynamic parameters and phase separation phenomena

Polysaccharides are a special class of natural polymers with great scientific and practical importance. Among these, xanthan is distinguished by a number of unique features, and can be found in various industrial and commercial products. The obtaining of xanthan involves an aseptic fermentation and a number of subsequent operations, and in the end the recovery of the polymer is required. The recovery of xanthan is currently performed through its precipitation in the presence of inferior aliphatic alcohols. Although from a practical point of view this process is wide spread, from theoretical point of view there are many insufficiently elucidated aspects on the thermodynamic and colloidal properties, and how they influence the phase separation phenomena.

In a number of studies reported in earlier stages [2011, 2014], the project team has investigated some of the thermodynamic properties of xanthan, and the conditions for the hydrogel formation of this polymer were also investigated.

In terms of thermodynamic aspect, finding theta condition (solvent, temperature) where the polymer-solvent interactions are canceled in the case of xanthan is a delicate problem. In the literature are not mentioned such studies. Building upon previous conclusions about the effect of the salt on the xanthan conformational parameters in aqueous solution [12,13], in this phase the studies were focused on the investigations of colloidal and thermodynamic characteristics of xanthan solutions and their correlation with the conditions where phase separation occurs.

An important parameter which influences the phase separation phenomena is the **thermodynamic quality of the solvent** dictated by the solvent/nonsolvent ratio or by the **temperature**. Other parameters that influence the occurrence of phase separation phenomena were also investigated: **polymer concentration** and **concentration of added salt** in aqueous solutions [14].

The theta composition of the water/ethanol mixture (solvent/nonsolvent) was determined using Elias method [15] by turbidimetric titration of xanthan solution in water with ethanol as nonsolvent. Elias method involves graphical representation of volume fraction of the nonsolvent corresponding to the first point where the xanthan solution becomes cloudy (ϕ_2^{CP}) depending on mass fraction corresponding to this point (c_p^{CP}). Extrapolation of ϕ_2^{CP} line according to c_p^{CP} at $c_p^{CP} = 0$ leads to a value of the volume fraction of ethanol corresponding to theta composition.

Based on data obtained from the dependence of turbidity on the salt concentration and the volume fraction of nonsolvent for different concentrations of xanthan, the conditions where phase separation occurs were determined (Figure 11).

These studies will be complemented by other thermodynamic investigations and the results will be submitted for publication in 2016.

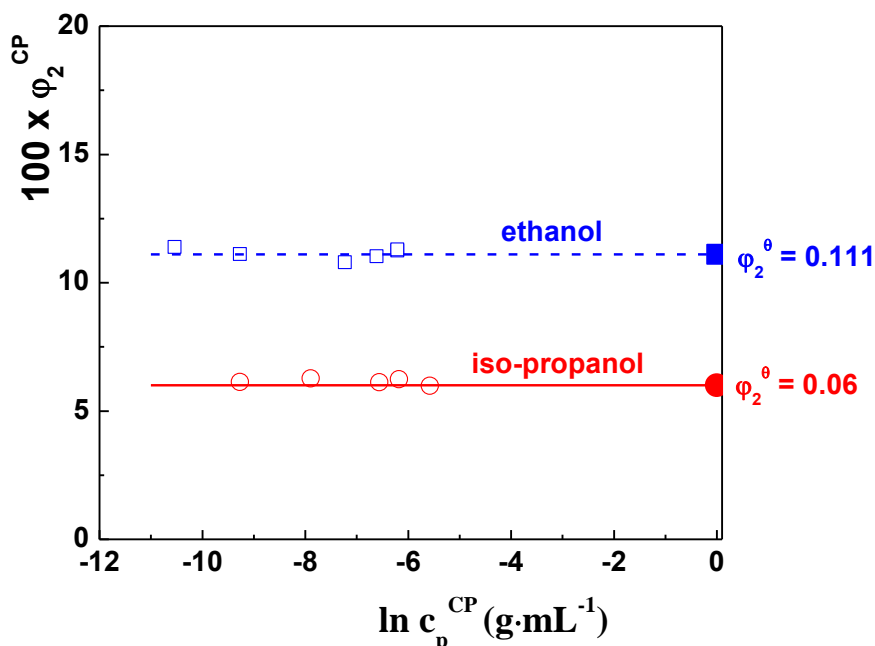


Figure 11. The determination of theta point for xanthan solutions based on data obtained from the investigation of the solutions turbidity in different thermodynamic conditions [14].

- In this phase of the project (2015), a number of smart polymeric materials based on natural, synthetic polymers and/or clay were obtained and their properties under different shear, temperature and pH conditions were investigated.
- Studies were performed regarding the phase separation phenomena for xanthan under different thermodynamic conditions.

References

1. M. Bercea, S. Morariu, [Rheological investigation of Pluronic F127/PVA mixtures in aqueous solution and gel state](#), *J. Hydrogels*, 2015 (accepted)
2. M. Bercea, L. E. Nita, S. Morariu, A. Chiriac, [In-situ gelling system based on Pluronic F127 and poly\(vinyl alcohol\) for smart biomaterials](#), *Rev. Roum. Chim.*, **60(7-8)**, 787–795 (2015)
3. L. C. P. Trong, M. Djabourov, A. Ponton, *J. Coll. Interface Sci.* **328(2)**, 278–287 (2008)
4. G. Wanka, H. Hoffmann, W. Ulbricht, *Macromolecules* **27(15)**, 4145–4159 (1994)
5. M. Bercea, S. Morariu, D. Rusu, *Soft Matter* **9(4)**, 1244–1253 (2013)
6. I. E. Lamatic, M. Bercea, and S. Morariu, *Rev. Roum. Chim.* **54(11-12)**, 981–986 (2009)
7. C. Guo, J. Wang, X. Liang, L. Cheng, H. Liu, *Sci. China Ser. B: Chem.*, **49**, 541–549 (2006)
8. [L. M. Gradinaru](#), C. Ciobanu, S. Vlad, [M. Bercea](#), [Rheological investigation of thermoreversible polyurethane hydrogels](#), *Rev. Roum. Chim.* under evaluation
9. M. Bercea, E.-L. Bibire, S. Morariu, M. Teodorescu, G. Carja, [pH influence on rheological and structural properties of chitosan/poly\(vinyl alcohol\)/layered double hydroxide composites](#), *European Polymer Journal*, **70(12)**, 147–156 (2015)

10. M. Bercea, E.-L. Bibire, S. Morariu, G. Carja, [Chitosan/PVA/LDH biocomposites with pH-sensitive properties](#), *International Journal of Polymeric Materials and Polymeric Biomaterials*, **64**, 628–636 (2015)
11. S. Morariu, M. Bercea, C.-E. Brunchi, [Effect of cryogenic treatment on the rheological properties of chitosan/poly\(vinyl alcohol\) hydrogels](#), *Industrial & Engineering Chemistry Research*, **54**, 1475–11482 (2015)
12. C.-E. Brunchi, S. Morariu, M. Bercea, Intrinsic viscosity and conformational parameters of xanthan in aqueous solutions: Salt addition effect, *Colloids and Surfaces B: Biointerfaces* **122**, 512–519 (2014)
13. Report for the project **PN-II-ID-PCE-2011-3-0199** (2014)
14. S. Morariu, unpublished data
15. H. G. Elias, *Makromol. Chem.* **50**, 1-19 (1961)

All objectives were fully realized and most results were used in manuscripts submitted to publication.

Results dissemination

- 8 papers were published in journals indexed by web of knowledge, the total **Impact Factor** being of **21.162**;
- 2 papers published in the first number of a new journal: – *Journal of Hydrogels* (American Scientific Publishers);
- 1 article accepted for publication in *Journal of Hydrogels*;
- 1 participation at a scientific event.

Project web page can be accessed at the following addresses:

<http://bercea300en.weebly.com> and <http://www.icmpp.ro/projects.html>